

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | |
|--|-----------|--|
| (51) International Patent Classification 5 : C08B 37/00 | A1 | (11) International Publication Number: WO 93/15116 (43) International Publication Date: 5 August 1993 (05.08.93) |
| (21) International Application Number: PCT/US93/00725 (22) International Filing Date: 27 January 1993 (27.01.93) (30) Priority data: 07/828,633 31 January 1992 (31.01.92) US (60) Parent Application or Grant (63) Related by Continuation US Filed on 07/828,633 (CON) 31 January 1992 (31.01.92) (71) Applicant (for all designated States except US): THE DOW CHEMICAL COMPANY [GB/GB]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (GB). | | (72) Inventors; and (75) Inventors/Applicants (for US only) : CHRISTENSEN, Ste- phen, B. [US/US]; 4410 Ottawa Street, Midland, MI 48642 (US). GROVER, Joseph, A. [US/US]; 1305 North Parkway, Midland, MI 48640 (US). (74) Agent: WARRICK, Noreen, D.; The Dow Chemical Com- pany, Patent Department, P.O. Box 1967, Midland, MI 48641-1967 (US). (81) Designated States: AU, BB, BG, BR, CA, FI, HU, JP, KR, LK, MG, MN, MW, NO, NZ, PL, RO, RU, SD, UA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG). Published <i>With international search report.</i> |
| (54) Title: PROCESS FOR REDUCING THE VISCOSITY OF NATURAL CARBOHYDRATE GUMS (57) Abstract This invention pertains to a process for reducing the viscosity of a hydrolyzable partially hydrated natural carbohydrate gum, e.g., guar gum, locust bean gum, and gum karaya, through a controlled acid hydrolysis thereof at a temperature between about 35 °C and about 100 °C. | | |

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | |
|----|--------------------------|----|---------------------------------------|----|--------------------------|
| AT | Austria | FR | France | MR | Mauritania |
| AU | Australia | GA | Gabon | MW | Malawi |
| BB | Barbados | GB | United Kingdom | NL | Netherlands |
| BE | Belgium | GN | Guinea | NO | Norway |
| BF | Burkina Faso | GR | Greece | NZ | New Zealand |
| BG | Bulgaria | HU | Hungary | PL | Poland |
| BJ | Benin | IE | Ireland | PT | Portugal |
| BR | Brazil | IT | Italy | RO | Romania |
| CA | Canada | JP | Japan | RU | Russian Federation |
| CF | Central African Republic | KP | Democratic People's Republic of Korea | SD | Sudan |
| CG | Congo | KR | Republic of Korea | SE | Sweden |
| CH | Switzerland | KZ | Kazakhstan | SK | Slovak Republic |
| CI | Côte d'Ivoire | LJ | Liechtenstein | SN | Senegal |
| CM | Cameroon | LK | Sri Lanka | SU | Soviet Union |
| CS | Czechoslovakia | LU | Luxembourg | TD | Chad |
| CZ | Czech Republic | MC | Monaco | TG | Togo |
| DE | Germany | MG | Madagascar | UA | Ukraine |
| DK | Denmark | ML | Mali | US | United States of America |
| ES | Spain | MN | Mongolia | VN | Viet Nam |
| FI | Finland | | | | |

PROCESS FOR REDUCING THE VISCOSITY OF NATURAL CARBOHYDRATE GUMS

This invention pertains to a process for reducing the viscosity of a hydrolyzable
5 partially hydrated natural carbohydrate gum.

A number of natural gums have been used in a variety of food and pharmaceutical applications. The utility of these gums has been limited in part by their general availability in only a narrow molecular weight range. Guar gum, for example, is a relatively high molecular weight gum. As a result, it may not be suitable for use in certain formulations,
10 since excessively high viscosities result. For instance, high molecular weight gums are generally not suitable for use in film coating applications, since most film coating applications require the use of solution concentrations of 10 percent or more to obtain sufficient film thickness. At these high concentrations, high molecular weight gums result in solutions so viscous that they cannot be handled by typical film coating equipment.

15 U.S. Patent 3,300,473, which issued on January 24, 1967, discloses a process for degrading a natural gum comprising: (1) impregnating a finely divided or pulverulent mass of the gum with a reactant capable of degrading or otherwise modifying the gum chemically, e.g., hydrochloric acid gas; (2) heating the impregnated material under vacuum and with a gradual increase in temperature to continuously decrease the water content until the material
20 is dehydrated so extensively that practically no moisture will evaporate from the mass in the ensuing treatments; (3) subjecting the material to an increased temperature in the absence of oxygen; and (4) cooling the material in the absence of oxygen. This process poses several disadvantages. Step 2 requires heating under vacuum to extensively dehydrate the impregnated gum. Steps 3 and 4 require heat treating the material in an oxygen free
25 environment. Such features add to the cost of the finished product.

U.S. Patent 2,553,485, which issued on May 15, 1951, discloses a process for producing low viscosity manno-galactan compositions comprising heating powdered manno-galactan material at high temperatures and in a substantially dry condition, optionally in the presence of an acid, e.g., gaseous hydrochloric acid. A 1 percent aqueous dispersion of the

resultant material is reported to have a viscosity of not more than 15 mPa-s at 30°C. It is reported to be desirable to carry out the degradation at the lowest temperature possible. It is reported that a suitable temperature range is from 115°C to 160°C. When an acid is present, the reported preferred temperature range is between 120°C and 140°C. The high temperatures contemplated suffer the disadvantage of adding to the cost of the finished product.

As set forth in "Dietary Fiber from Guar Plant Seed", authored by Hidehisa Takahashi of Taiyo Kagaku Company, Ltd., it is known to enzymatically digest guar gum with beta-D-mannanase produced by Aspergillus niger to obtain a purified low molecular weight low viscosity guar gum. See, also, Food Engineering, April 1990, page 34.

Those in industry would find great advantage in a process for reducing the viscosity of natural gums which does not involve the disadvantages of the prior art. In particular, the advantageous process would not involve heating the gum to the point of dehydration, heating under vacuum, heating at temperatures in excess of 100°C, and/or cooling in an oxygen free environment. Further, the advantageous process would utilize readily available and inexpensive reagents, e.g., hydrochloric acid, rather than, e.g., enzymes.

Accordingly, this invention pertains to a process for reducing the viscosity of a hydrolyzable partially hydrated natural carbohydrate parent gum, comprising:

- (a) contacting the partially hydrated parent gum with an acid at a temperature between 35°C to 100°C to form a hydrated precursor;
- (b) purging the hydrated precursor with a purge gas to at least partially remove residual acid; and
- (c) neutralizing any residual acid not removed by the purging of step (b) with a base to form a product gum,

whereby a 2 weight percent aqueous dispersion of the product gum has a viscosity at 20°C substantially less than the viscosity at 20°C of a 2 weight percent aqueous dispersion of the parent gum.

These reduced molecular weight versions of natural gums may be useful in film coating applications, as excipients, as binders, as food rheology modifiers, and as a source of dietary fiber, as well as having other uses.

The following detailed description more fully discusses various embodiments of the subject invention.

Currently, there is a great interest in natural hydrophilic gums as possible film-formers and as a source of dietary fiber to impart health benefits. To be useful in film-forming applications, or to be palatable in food applications, however, the fiber or gum must be fairly low in viscosity. Most natural gums, such as guar gum, are too viscous for these applications.

The subject process is useful to produce low viscosity samples of partially hydrated hydrolyzable natural carbohydrate gums such as guar gum, locust bean gum, and gum karaya. In particular, the subject process results in a product gum, wherein the viscosity of a 2 weight

percent aqueous dispersion of the product gum is substantially less than that of the parent gum. As used herein, the term "viscosity substantially less than" means that the viscosity at 20°C of a 2 weight percent aqueous dispersion of the product gum is at least about 50 percent less than the viscosity at 20°C of a 2 weight percent aqueous dispersion of the parent gum at the applicable shear rate. More preferably, the viscosity at 20°C of a 2 weight percent aqueous dispersion of the product gum is at least about 75 percent less than the viscosity at 20°C of a 2 weight percent aqueous dispersion of the parent gum at the applicable shear rate. Even more preferably, the viscosity at 20°C of a 2 weight percent aqueous dispersion of the product gum is at least about 95 percent less than the viscosity at 20°C of a 2 weight percent aqueous dispersion of the parent gum at the applicable shear rate.

The inventive process usefully provides gums wherein the viscosity of a 2 percent aqueous dispersion thereof is less than about 25 mPa-s, as measured using a Brookfield cone and plate viscometer at a temperature of 20°C and at a shear rate between about 5 sec⁻¹ and about 120 sec⁻¹. The inventive process further usefully provides gums wherein the viscosity of a 2 percent aqueous dispersion thereof is less than about 10 mPa-s, as measured using a Brookfield cone and plate viscometer at a temperature of 20°C and at a shear rate between 5 sec⁻¹ and 120 sec⁻¹. The inventive process further usefully provides gums wherein the viscosity of a 2 percent aqueous dispersion thereof is less than about 5 mPa-s, as measured using a Brookfield cone and plate viscometer at a temperature of 20°C and at a shear rate between 5 sec⁻¹ and 120 sec⁻¹.

Preferred gums are hydrolyzable. As used herein, "hydrolyzable" means that the selected gum can be at least partially depolymerized to lower molecular weight units by acid hydrolysis. Preferred gums will be hydrolyzable without the addition of more than about 0.1 moles of acid/100 grams of gum. More preferred gums will be hydrolyzable without the addition of more than about 0.03 moles of acid/100 grams of gum.

Preferred gums are partially hydrated. As used herein, "partially hydrated" means containing water of hydration sufficient to facilitate the acid hydrolysis reaction, yet insufficient to deleteriously affect properties. The presence of between 1 and 5 weight percent water of hydration facilitates the acid hydrolysis reaction. The presence of between 6 and 20 weight percent water of hydration, while not deleterious to the reaction, is less preferred due to the need to later remove such excess water to minimize packing together of the product gum particles. The presence of more than about 20 weight percent water of hydration is not preferred due to the increased cost of later removal, i.e., partial dehydration.

As used herein, "natural carbohydrate" gum means a gum originating from a naturally occurring and harvested source, as opposed to a chemically synthesized gum. Suitable natural carbohydrate gums include, e.g., guar gum, locust bean gum, and gum karaya.

The inventive process involves a controlled acid hydrolysis of the desired partially hydrated hydrolyzable natural carbohydrate gum. In particular, guar gum, locust bean gum,

and gum karaya have been successfully modified by adding a sufficient amount of an acid to the gum, holding the acidified gum for a sufficient time at a suitable temperature, and then removing and/or neutralizing the residual acid. Lower molecular weight versions of the gums result, and dispersions of these reduced molecular weight gums exhibit substantially lower viscosities than dispersions of the parent gums at the same concentration and at the same temperature and applicable shear rate.

Suitable acids will serve to hydrolyze the gum, without otherwise destroying its molecular structure. While any protic acid source would hydrolyze the gum, e.g. organic acids, preferred acids include mineral acids such as hydrochloric acid, hydrobromic acid, and sulfuric acid. Preferably, the acid will be hydrochloric acid.

As used herein, "sufficient amount of an acid" means an amount of acid useful to form a product gum, wherein the viscosity of a 2 weight percent aqueous dispersion thereof is substantially less than that of a 2 weight percent aqueous dispersion of the parent gum. Preferably, the acid will be provided at a use level of less than about 0.1 mole of H^+ ions/100 grams of the selected gum. More preferably, the acid will be provided at a use level of less than about 0.03 moles of H^+ ions/100 grams of the selected gum.

Preferably, the acid will closely contact the gum to facilitate a substantially complete reaction. Accordingly, gaseous hydrochloric acid is a preferred acid, as it can permeate between the gum particles. Further, gaseous hydrochloric acid affords the advantage of not adding additional water to the system, which would later need to be removed to produce a powdered low viscosity gum. Should the economics involved with water removal not be problematic, aqueous acid solutions may be used rather than gaseous acid. Preferably, the use of such liquids would be accompanied by suitable mixing to facilitate the desired acid-gum contact.

Suitable reaction temperatures are those which would promote the hydrolysis reaction. Preferred temperatures are between 35°C and 100°C. More preferred temperatures are between 45°C and 80°C.

As used herein, the term contacting "for a suitable period of time" means that the hydrolysis reaction should be allowed to proceed to the desired degree of completion, i.e., for a time sufficient to attain the desired reduction in viscosity. In general, the longer the contact, the greater the degree of viscosity reduction. As set forth below in the examples, contacting guar gum in the presence of hydrogen chloride gas for 26 hours at a temperature between about 45°C and about 50°C produces a low viscosity gum. Contacting guar gum with hydrogen chloride gas for about 18 hours at a temperature of about 60°C, contacting gum karaya with hydrogen chloride gas for about 6 hours at a temperature of about 60°C, and contacting locust bean gum with hydrogen chloride gas for about 48 hours at a temperature of about 60°C, likewise produce suitable low viscosity gums. From an economic perspective, preferred contacting times are less than about 48 hours.

Contacting the hydrated gum with an acid at a suitable temperature for a suitable time, as described above, forms a hydrated precursor. As used herein, "hydrated precursor" means the hydrolyzed version of the hydrolyzable, partially hydrated, natural carbohydrate gum. During the contemplated acid hydrolysis reaction, a portion of the water of hydration contained in the parent gum is consumed. There is no perceived advantage to further driving off water of hydration remaining in the hydrated precursor.

Preferably, the hydrated precursor will be purged with an inert purge gas, to at least partially remove residual acid. As used herein, "inert" means non-reactive with the hydrated precursor. Preferred purge gases include air and nitrogen. Suitable purge times will depend on, e.g., the desired extent to which the acid is to be removed, the flow rate of the gas, whether the hydrated precursor is agitated during purging, etc. The selection of suitable flow rates and the implementation of agitation are well understood by those skilled in the art. Purging is typically conducted for between about 10 minutes and about 4 hours. From an economics standpoint, purging should preferably be accomplished within about one hour.

Acid remaining in the product upon purging may be neutralized with an appropriate base. Preferred bases are weak bases suitable to form a self-buffering system, e.g., phosphates, organic acid salts, etc., as well-known to those having skill in the art. Particularly preferred bases include alkali metal carbonates and bicarbonates due to the formation of carbon dioxide upon neutralization. More particularly preferred bases include sodium or potassium bicarbonate or carbonate. A most preferred base is sodium bicarbonate.

The selected base will be added in an amount to result in a product gum have a pH appropriate for the end use contemplated. The adjustment of pH of an acidic product using an appropriate amount of an appropriate base is well-understood by those skilled in the art. Should a neutral product gum be desired, i.e., a product gum having a pH of 7, e.g., for gums to be consumed, the selected base will preferably be added in a stoichiometric amount. The stoichiometric amount may be determined by titrating the purged product to determine the amount of residual acid. To facilitate a full neutralization, the purged hydrolyzed natural carbohydrate gum and the selected base are thoroughly mixed together.

The viscosity of a 2 weight percent aqueous dispersion of the product gum may be conveniently measured at a temperature of 20°C using a Brookfield cone and plate viscometer, available from Brookfield Engineering Co., Inc. (Stoughton, MA). The subject process provides gums wherein the viscosity of a 2 weight percent aqueous dispersion thereof is less than about 100 mPa-s at a shear rate between about 5 sec⁻¹ and about 60 sec⁻¹. The subject invention produces product guar gum wherein the viscosity of a 2 weight percent aqueous dispersion thereof is less than about 10 mPa-s, as compared to a viscosity of a 2 weight percent aqueous dispersion of the parent guar gum in excess of about 10,000 mPa-s. The subject invention produces product locust bean gum wherein the viscosity of a 2 weight percent aqueous dispersion thereof is less than about 5 mPa-s, as compared to a viscosity of a 2 weight percent

aqueous dispersion of the parent locust bean gum in excess of about 10,000 mPa-s. The subject invention produces product gum karaya wherein the viscosity of a 2 weight percent aqueous dispersion thereof is about 25 mPa-s as compared a viscosity of a 2 weight percent aqueous dispersion of the parent gum in excess of about 500 mPa-s.

5 The following examples are provided for the purpose of explanation rather than limitation.

Example 1

One kilogram of guar gum powder was loaded into a one gallon (3.8 L) closed container. Using a syringe, 6500 cm³ of hydrogen chloride gas was introduced to the container through a septum, with mixing. The contents were mixed continuously for 26 hours at a temperature between 45°C and 50°C. The product was purged with air for one hour, and the amount of remaining acid was determined by titration of a sample with base. The purged guar gum was thoroughly mixed with a stoichiometric amount of powdered sodium bicarbonate to neutralize the residual acid. The viscosity of 2 weight percent aqueous dispersion of a sample processed in this manner, measured using a Brookfield cone and plate viscometer, was 72 mPa-s at 20°C and at a shear rate of 6.0 sec⁻¹. This compares to a measured viscosity of 18,756 mPa-s at 20°C and at a shear rate of 5.0 sec⁻¹ for a 2 percent aqueous dispersion of the unmodified hydrated gum.

Example 2

20 One hundred grams of a gum as specified in the following Table One were loaded into a 1000 mL round bottom flask that was then mounted on a Büchi rotary evaporator. The assembly was fit to provide an all glass system that could be evacuated, vented, and charged with a gas. The flask containing the gum was evacuated for 5 minutes using an aspirator. Using a 1000 mL syringe, an amount of hydrogen chloride gas as specified in the following Table One was introduced into the flask with mixing. On the scale of this example, a 1 percent by weight charge of hydrogen chloride gas corresponds to 650 mL. Air was then drawn into the system to equilibrate to atmospheric pressure. The inlet valve was then closed. The closed flask was heated in a 60°C water bath with rotation for the indicated time. After reaction, the sample was cooled and the residual hydrogen chloride was neutralized with a stoichiometric amount of sodium bicarbonate. Viscosities of 2 percent aqueous dispersions of the hydrated parent gums and the product gums were measured using a Brookfield cone and plate viscometer at 20°C. The data are set forth in the following Table One.

35 The process as applied in Example 2 to xanthan gum and sodium alginate, is not a part of the present invention, due to the inadequate viscosity reductions achieved. While not wishing to be bound by theory, it is believed that the resistance of xanthan gum and sodium alginate to acid hydrolysis may be attributed to the greater number of carboxylate functional groups present in the molecular structures thereof which serve to buffer or neutralize an equivalent amount of added acid.

Table One

| | Guar Gum | Gum Karaya | Locust Bean Gum | Xanthan Gum | Sodium Alginate |
|---|---------------------|-----------------------|----------------------------|------------------------|----------------------------|
| Initial viscosity (mPa·s) | 10,420 | 528 | 10,970 | 11,010 | 177 |
| Applicable Shear Rate (sec⁻¹) | 10 | 12 | 10 | 2 | 60 |
| Added HCl (wt %) | 0.9 | 1 | 1 | 3 | 1 |
| Reaction time (hours) | 18 | 6 | 48 | 6 | 24 |
| Final viscosity (mPa·s) | 8.4 | 25 | 2.0 | 20,940 | 151 |
| Applicable shear rate (sec⁻¹) | 60 | 12 | 120 | 2 | 60 |

15 The above sets forth particular embodiments of the subject invention. Obvious variations will be apparent to those skilled in the art. Accordingly, the scope of this invention should be determined only by reference to the appended claims.

20

25

30

35

1. A process for reducing the viscosity of a hydrolyzable partially hydrated natural carbohydrate parent gum comprising:
 - 5 (a) contacting the partially hydrated parent gum with a sufficient amount of an acid at a temperature between about 35°C and about 100°C to form a hydrated precursor;
 - (b) purging the hydrated precursor with a purged gas to at least partially remove residual acid; and
 - 10 (c) neutralizing any residual acid not removed by the purging of step (b) with a base to form a product gum,whereby a 2 percent aqueous dispersion of the product gum has a viscosity substantially less than the viscosity of a 2 percent aqueous dispersion of the parent gum.
2. The process of Claim 1, wherein the partially hydrated parent gum is guar
15 gum, locust bean gum, or gum karaya.
3. The process of Claim 1, wherein the partially hydrated parent gum contains between about 1 and about 20 weight percent water of hydration.
4. The process of Claim 1, wherein the partially hydrated parent gum contains between about 1 and about 5 weight percent water of hydration.
- 20 5. The process of Claim 1, wherein the acid comprises a mineral acid.
6. The process of Claim 4, wherein the acid is a gas at the point of contacting.
7. The process of Claim 4, wherein the acid comprises gaseous hydrogen chloride.
8. The process of Claim 1, wherein the viscosity of the 2 percent aqueous
25 dispersion of the product is less than about 100 mPa·s at a temperature of about 20°C and at a shear rate between about 10 and about 120 sec⁻¹, as measured using a Brookfield cone and plate viscometer.
9. The process of Claim 1, wherein the viscosity of the 2 percent aqueous dispersion of the product is less than about 25 mPa·s at a temperature of about 20°C and at a

shear rate between about 10 and about 120 sec⁻¹, as measured using a Brookfield cone and plate viscometer.

10. The process of Claim 9, wherein the partially hydrated parent gum is guar gum, locust bean gum, or gum karaya.

5 11. The process of Claim 1, wherein the viscosity of the 2 percent aqueous dispersion of the product is less than about 10 mPa·s at a temperature of about 20°C and at a shear rate between about 10 and about 120 sec⁻¹, as measured using a Brookfield cone and plate viscometer.

12. The process of Claim 11, wherein the parent gum is guar gum or locust
10 bean gum.

13. The process of Claim 1, wherein the viscosity of the 2 percent aqueous dispersion of the product is less than about 5 mPa·s at a temperature of about 20°C and at a shear rate between about 10 and about 120 sec⁻¹, as measured using a Brookfield cone and plate viscometer.

15 14. The process of Claim 12, wherein the partially hydrated parent gum is locust bean gum.

15. The process of Claim 1, wherein the purge gas is air or nitrogen.

16. The process of Claim 1, wherein the neutralizing comprises titrating the
purged hydrated precursor to determine the concentration of the residual acid, and adding a
20 stoichiometric amount of the base to completely neutralize the residual acid.

17. The process of Claim 1, wherein the base is sodium bicarbonate, sodium carbonate, potassium bicarbonate or potassium carbonate.

18. The process of Claim 1, wherein the base comprises sodium bicarbonate.

25

30

35

| | | |
|--|---|-------------------------------------|
| I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ | | |
| According to International Patent Classification (IPC) or to both National Classification and IPC Int.C1. 5 C08B37/00 | | |
| II. FIELDS SEARCHED | | |
| Minimum Documentation Searched ⁷ | | |
| Classification System | Classification Symbols | |
| Int.C1. 5 | C08B | |
| Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸ | | |
| III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ | | |
| Category ¹⁰ | Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹² | Relevant to Claim No. ¹³ |
| Y | DATABASE WPI Section Ch, Week 7507, Derwent Publications Ltd., London, GB; Class A, AN 75-12020W & NL,A,7 413 972 (MOBIL OIL CORP.) 31 January 1975 see abstract --- | 1,2,5-7 |
| Y | FR,A,974 862 (J. SANTAMARIA ZAMORA) 27 February 1951 see page 1, left column, line 1 - line 3 see page 1, left column, line 40 - right column, line 26 see page 2, left column, line 56 - right column, line 19 --- -/--- | 1,2,5-7 |
| <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> | | |
| IV. CERTIFICATION | | |
| Date of the Actual Completion of the International Search | Date of Mailing of this International Search Report | |
| 27 APRIL 1993 | 10. 02. 93 | |
| International Searching Authority | Signature of Authorized Officer | |
| EUROPEAN PATENT OFFICE | MAZET J.-F. | |

| III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET) | | |
|--|--|-----------------------|
| Category * | Citation of Document, with indication, where appropriate, of the relevant passages | Relevant to Claim No. |
| A | US,A,2 553 485 (J.W. SWANSON) 15 May 1951 cited in the application see examples II,III ----- | 1 |

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9300725
SA 69686

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 27/04/93

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| FR-A-974862 | | None | |
| US-A-2553485 | | None | |